

The University of Chicago

STUDIES ON SPECTROGRAPHIC
CHEMICAL ANALYSIS

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

1938

By

OSVALDO RAMIREZ-TORRES

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INTRODUCTION

The unique applicability of spectrographic methods for certain types of chemical analysis, in particular to the determination of small traces in biological and botanical material, have led to this study. The objectives are:

1. A thorough understanding and testing of the available spectrographic equipment.
2. Selection of conditions generally suitable for chemical analysis.
3. Investigation of the best technique for qualitative analysis.
4. Development of charts for use in qualitative analysis.
5. General study of the methods of quantitative spectrographic analysis.
6. Development of quantitative method for silica determination.

This investigation has been confined to applications of the d.c. arc. There are, however, several methods of spectroscopic excitation in widespread use. A survey of the literature indicates that the most generally useful excitation methods are the d.c. arc, the a.c. arc, and the spark. The a.c. arc¹ has proved to have high sensitivity in certain commercial applications and the high tension spark is generally used for samples which are metals or alloys. The d.c. arc seemed most promising for general chemical analysis because it is suitable for use with powders, metals, ashed material, solutions, or in general with any material which can be introduced into a crater in a carbon electrode. Accordingly the use of the d.c. arc was selected for this investigation, and since this arc often leads to a fractional distillation of constituents from the sample, methods have in general been sought for complete volatilization of the sample during the course of photographing the spectra. Because of that the use of graphite electrodes has been followed in all experiments since the use of metal electrodes often limits the tempera-

¹Duffendack and Thomson, Proc. Am. Soc. Testing Materials, 36, Part II, 301 (1936).

ture attainable in the arc. Graphite electrodes are also advantageous because their low cost permits use of a fresh electrode for each sample.

CHAPTER I

APPARATUS, ELECTRODES AND ILLUMINATION SYSTEM

1. Apparatus

All of the present work has been done with a Hilger large quartz spectrograph. This instrument is of the Littrow form and gives a much higher dispersion than is attainable with other types of quartz prism instruments. In fact several of the studies made in qualitative analysis could not have been made with a smaller dispersion instrument since many metal samples give a very complex spectra in which lines of trace elements present may be masked by weak lines of the matrix elements unless the highest possible dispersion is used.

An optical bench was securely mounted on the base of the instrument at right angle to the slit jaws. The bench consisted of a rigid square bar which held a number of moveable socket clamps. All lenses and parts of the illumination system were mounted on 5/8 inch brass rods which fitted the clamps.

Another essential accessory was an exhaust hood which enclosed the arc. This hood is very necessary for removing metal vapors and the nitrogen oxides, for shielding the arc from draughts, and for keeping the operator away from the brilliant light of the arc. The arcing can be constantly observed through a glass filter window, a 2 x 4-1/4 inches Noviweld glass plate,² Bureau of Standards density formula No. 14, placed on one side of the hood. This glass absorbs all the ultra-violet and almost all the infra-red rays, and although it only transmits a small portion of the visible light, yet it permits the white hot electrodes to be seen.

The hood was constructed from a single metal sheet bent into a wide ellipse and soldered to top and bottom plates. The back was left open, in order to permit ready adjustment of the electrodes during operation. On the front a small opening per-

²American Optical Co., "Industrial Eye Protection Catalog," 1935, p. 19.

mits light from the arc to reach the slit. The arrangement of optical bench and hood is shown in Figure 1.

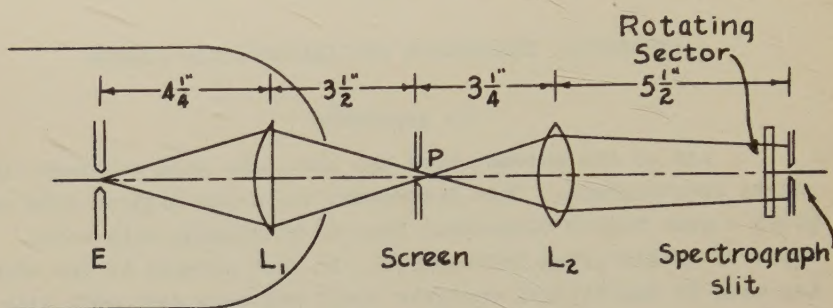


Fig. 1

An electrode holder was constructed as shown in Figure 2. This permits vertical adjustment of each electrode by means of a rack and pinion, and horizontal displacement by rotation of the entire stand. Both adjustments are necessary during every exposure. The side arms which carry the electrodes are insulated from the body of the holder by transite blocks. At the end of each arm there is a $\frac{1}{4}$ in. hole in which a stainless steel adapter, A, is mounted by means of a set screw. The end of the adapter forms a clamp which holds the electrode securely. Separate adapters are used for each size electrode. Use of the adapter permits marked economy for in most analyses it is not necessary to use electrodes of length greater than $\frac{5}{8}$ to 1 in., whereas without the adapter it is necessary to make the electrode $1\frac{1}{2}$ to 2 in. long. An adjustable pointer, P, is useful for setting the electrodes before an exposure.

The arc was operated from a 220 volt source, since use of 110 volts was found to give more wandering. A resistance in series was used to regulate the current to 10 amp. By means of a switch an additional resistance was cut in when it was desired to reduce the current to 4-5 amp.

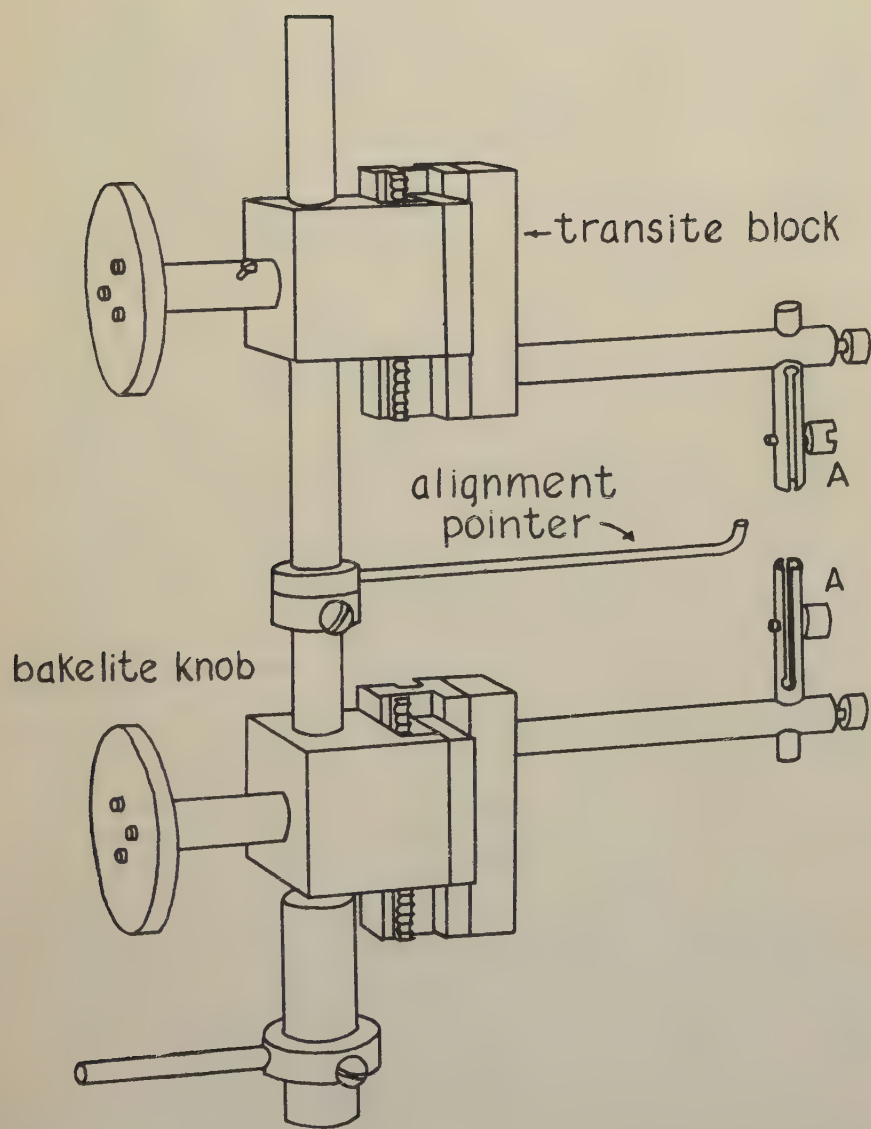


Fig.2. Electrode stand

2. Electrodes and Their Purification

Acheson graphite electrodes were used in all experiments except those which required complete absence of silica. For the latter special spectroscopically pure electrodes prepared by the Dow Chemical Company were used. The Dow electrodes give no trace of silica lines when used under the conditions employed in the silica determinations. Three sizes of electrodes are used, 1/8 in., 3/16 in., and 1/4 in. As furnished by the manufacturer the Acheson electrodes contain many impurities and various purification methods have been tested. The one finally used, as most convenient, is as follows: The electrodes are cut to the desired length and the crater is drilled according to the use to be made of the electrode. A batch of several hundred lengths is placed in a large Erlenmeyer flask fitted with a reflux condenser, a mixture of equal parts of hydrochloric and nitric acids is added and the solution is refluxed for several hours. The acid is poured off, the electrodes washed several times by decantation, and the acid treatment is repeated. After removal of the acid, and several washings, the electrodes are covered with redistilled hydrochloric acid and refluxed for several hours. Repeated washing with pure water, refluxing each portion for a time, completes the purification. The well-washed electrodes are dried in an oven and stored until needed. Spectra from one minute exposures of the treated electrodes show the presence of silica, boron, slight traces of calcium, magnesium, and copper. Somewhat purer electrodes can be obtained by giving the acid treated electrode a preliminary arcing of one minute, with the electrode as the positive pole. This arcing removes much of the silica, together with practically all the calcium magnesium and copper, but has the disadvantage that the arced electrode is left in a much more porous condition than the unarced electrode.

3. Illumination System

A study was made of the conditions best suited for illumination of the slit. In general, high intensity is not a requirement since considerable time is required for complete volatilization of the sample and the intensity must be reduced by a rotating sector. Therefore the foremost requirement was that the slit be

uniformly lighted from top to bottom and that all the light passing the slit fall onto the collimator lens so that irregularities in the arc would not cause unequal lighting during an exposure. Further it was found that screening out the light from the incandescent electrodes greatly reduces the background on the plate. Consequently the arrangement of Twyman and Simeon³ was employed. This arrangement is shown in Figure 1. The adjustment of this system is quite critical if best results are to be obtained, and the following method is recommended: The arc is placed near the focus of a short-focus quartz lens, L_1 , so that the image of the arc is brought to a focus near the point P. A second convex quartz lens, L_2 , is placed so that the point P is near its focal length. Then, by slight changes in the position of this lens the light beam can be made slightly convergent, parallel, or slightly divergent. Best results are obtained with the light parallel or slightly convergent. The spectrograph slit is now opened wide and the position of L_2 changed until the beam fills the collimator lens of the spectrograph. Finally the screen, S, is so placed that the image of the electrodes is sharply defined. The screen opening is adjusted until the desired portion of the arc passes through. In general the opening is about 3 mm. in height. The screen serves a threefold purpose; (a) it selects the desired portion of the arc, thus giving more uniform illumination of the slit, (b) it provides the operator with a visible guide as to the position of the two electrodes and their separation during the exposure, and (c) it protects the slit from the visible light emitted by the glowing electrodes. While the various distances will depend upon the focal lengths of the two lenses, the distances given in Figure 1 are generally favorable for the setup is such as to leave sufficient space between L_2 and the slit for the introduction of such rotating sectors as may be needed.

With the slit illumination as described, the spectrograph was focussed for the regions 2410-3305 Å and 3225-8000 Å according to the procedure given by the manufacturer, using an iron arc for illumination. Considerable difficulty was encountered in this process for the lines at first obtained were not sharp images of the slit. Flat lines were finally obtained after complete readjusting of the spectrograph. This process included removal and

³Twyman and Simeon, Trans. Opt. Soc., 31, 179 (1929-30).

cleaning of the right angle prism and decreasing the tension exerted on the main prism by its set screw. In addition, the collimator lens was tightened in its holder. After this readjustment the lines obtained were very flat, even when as wide as 0.05 mm. and it was further noted that the spectrograph focus was no longer so highly dependent upon temperature as formerly. As now operated a temperature change of 5° C does not require refocussing to give sharp lines.

The spectrograph, like many Littrow type instruments, caused much trouble due to flare spots reflected from the collimator lens. These spots caused a non-uniform blackening of the plate at a point several millimeters above the point at which the spectra were incident. Various means were unsuccessfully tried for the elimination of this condition, including tilting of the collimator lens, but little was accomplished until a removable screen was constructed to shield the upper 3 mm. of the camera opening. Use of this screen permits spectra from only the central 2 mm. of the slit height, but with this limitation one may obtain as many as 36-2 mm. spectra on a single plate 4 x 10 in., without any fogging of one spectrum by another. The procedure is to set a wedge slide over the slit to give only a 2 mm. height, and to move the plate carrier a distance of 2-2.5 mm. between successive exposures.

CHAPTER II

QUALITATIVE ANALYSIS

A large portion of the time spent in this investigation was devoted to a study of qualitative analysis. Although current literature contains numerous publications on quantitative analysis comparatively little attention has been given to qualitative analysis. It became apparent early in this study that successful qualitative analysis demands as much in the way of skilful technique as quantitative analysis. Among the points studied were:

1. Possibilities of using existing spectral Atlases for qualitative purposes.
2. Construction of a wave length scale for the rapid identification of spectral lines.
3. Methods for arcing various types of samples and the proper size of electrode and depth of crater for best results with each sample.
4. The sensitivity of detection for various elements.

1. Use of Existing Spectral Atlases

It is a relatively simple matter to test a sample by means of the spectroscope specifically for the presence or absence of a given element or elements, but it proves to be quite a task to carry out a qualitative analysis of a complex spectrum with the view of determining the elements which gave rise to it. Although a single spectral line is sufficient to identify an element, approximate coincidences may often cause misidentifications, and to guard against this at least two or three lines should be checked. A complete classification of all lines making up a complex spectrum, that is the determination of their exact wavelengths, etc., would make spectroscopic qualitative analysis unavailable for practical purposes. A more rapid procedure must be sought, and it seems that the use of enlarged scales and enlarged comparison spectra onto which the spectra to be analyzed could be projected would be a marked advance toward the goal. We have come across four very important contributions to the solution of the problem along this line, viz.:

- I. "Atlas typischer Spektren," J. M. Eder and E. Valenta, A. Hölder, Wien, 1928. Beside useful condensed tables of arc, flame, and spark spectra, it contains very good reproductions of the prism and grating spectra of sixty-seven elements.
- II. "Atlas de Spectres D'Arc," Jacques Bardet, Gaston Doin et C^{ie}, Paris, 1926. This work consists of forty-eight plates, divided into six series. The first series comprises the grating spectra of the common metals, and the other five contain the spectra of these metals classified into analytical groups, as for example, series B consisting of the combined spectra of Ni, Co, Cr, and Mn. The grating spectra of the iron arc is also included, covering the region $\lambda 2500$ to $\lambda 3500 \text{ \AA}^{\circ}$.
- III. "Atlas der leztzten Linien der wichtigsten Elemente," Fritz Löwe, Theodor Steinkopff, Dresden and Leipzig, 1936. Spark spectra of forty-four elements on carbon electrodes. Reproductions of prism spectra.
- IV. Sensitive Arc Lines of fifty elements. J. W. Ryde & H. G. Jenkins, Adam Hilger, Ltd., London, 1929, 1935. A set of enlargements prepared from photographs of the prism spectra of these elements is furnished by the publishers to be used in connection with this table of ultimate lines.

Although these publications, particularly Nos. II and IV, were found to be very useful in connection with qualitative analysis, yet they were not all that could be desired for our purposes, especially for the preliminary examination of spectra. Bardet's Atlas has the disadvantage that the drawings (in this work spectra are drawn, not reproduced), are from grating spectra. The reproductions in the Eder and de Valenta Atlas, as well as those in Löwe's book, are of small size. So it was decided to prepare a large wavelength scale onto which our plates could be projected at a convenient magnification.

2. Construction of the Wave Length Scale

A lantern (Spencer Delineascope) was arranged to project horizontally onto a moveable screen. The screen consisted of a drawing board mounted on a heavy base which could be moved horizontally with reference to the lantern. On this board, at the height of the projection mirror, there is a slot to carry the cardboard strips, $6\text{-}1/2 \times 25 \text{ in.}$, on which the scale is to be drawn. The lantern is fitted with a mask having an opening $13 \times 50 \text{ mm.}$ so arranged that only the central portion of the lens system is used for projection. This was necessary because if pro-

jection is made from different portions of the field the magnification varies throughout a single spectrum and reproducibility can only be obtained by always projecting in the same manner. The magnification is controlled by the distance from lantern to screen, which can be varied from 5-8 feet.

The first operation in preparing the scale is to identify iron arc lines at convenient intervals. This is most easily done by projecting the iron spectrum onto the drawings of Bardet's tables, varying the magnification so that coincidence is obtained over a short interval. Selected lines are marked and the wave length confirmed by reference to Kayser's tables. After this step the spectrum with the identified lines is projected on a strip of a high quality cross sectional paper. Magnification (approx. $\times 13$), and focus conditions are kept constant from here on until the whole scale is finished. The centers of the identified lines are very carefully marked on the cross sectional paper and their wave lengths recorded there too. This procedure is repeated until the spectral region $\lambda 2500$ to $\lambda 5600$ is covered in sections 24" long.

For each section a wave length vs. dispersion curve is traced on the same kind of paper as that used for marking the lines. The points in the curve are plotted directly from the position of the centers of the spectral lines in the projected scale sections as abscissas, and their corresponding wave lengths as ordinates. Since there are no distances to be measured, or measurements to be reproduced in transferring from one paper to the other the plotting lacks the errors accompanying such procedures. Irregularities in the ruling of the paper do not introduce serious errors because the strips on which the lines are marked are cut from the base of the sheets of paper on which the curves are to be traced afterwards. During the plotting the vertical rulings are brought back to coincide with their original positions. All points fell on a very smooth curve.

The scale is now made by moving the strip of cross sectional paper along its corresponding curve section. Abscissas corresponding to points 5 Ångströms apart in the region $\lambda 2500$ to $\lambda 3200$ and to 10 Å in the region $\lambda 3200$ to $\lambda 5600$ are marked on it. These marks which constitute the actual 5 or 10 Å scale divisions are transferred to cardboard pieces, where the scale is finally drawn. These divisions are further subdivided into five equal

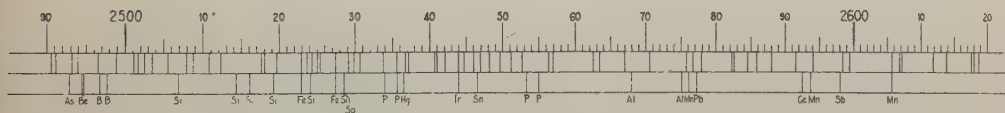
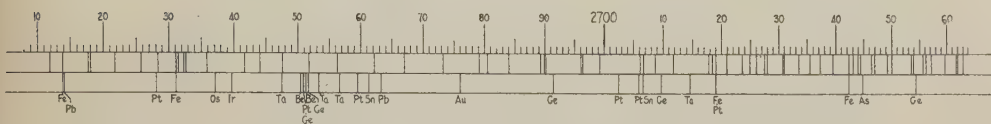
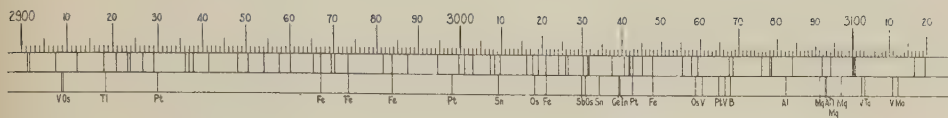
parts up to the $\lambda 4000$ section, and into two parts for the rest of the scale, corresponding to 1, 2 and 5 Ångstroms subdivisions, respectively. No sensible error is introduced by this procedure since the curve between points so close to each other was almost a straight line.

The final scale consists of nine sections, each section covering the following spectral regions:

Scale No. 1:	$\lambda 2490 - \lambda 2620$, 1 Å divisions
	60 cms. (23-1/2") long
	Ave. dispersion 4.5 mm. per Å
" " 2:	$\lambda 2610 - \lambda 2760$, 1 Å divisions
	58 cms. (22-1/2") long
	Ave. dispersion, 4 mm. per Å
" " 3:	$\lambda 2740 - \lambda 2920$, 1 Å divisions
	57 cms. (22") long
	Ave. dispersion, 3 mm. per Å
" " 4:	$\lambda 2900 - \lambda 3120$, 1 Å divisions
	57 cms. (22") long
	Ave. dispersion, 2.5 mm. per Å
" " 5:	$\lambda 3070 - \lambda 3280$, 1 Å divisions
	30 cms. (12") long
	Ave. dispersion, 2.2 mm. per Å
" " 6:	$\lambda 3270 - \lambda 3590$, 2 Å divisions
	57 cms. (22-1/2") long
	Ave. dispersion, 1.8 mm. per Å
" " 7:	$\lambda 3590 - \lambda 4050$, 2 Å divisions
	59 cms. (23") long
	Ave. dispersion, 1.3 mm. per Å
" " 8:	$\lambda 4040 - \lambda 4740$, 5 Å divisions
	59 cms. (23") long
	Ave. dispersion .8 mm. per Å
" " 9:	$\lambda 4730 - \lambda 5620$, 5 Å divisions
	56 cms. (22") long
	Ave. dispersion 0.6 mm. per Å

Net scale length approximately 15 feet

Three printings appear on this scale. The top part is the wave length scale proper, the central one contains the most important iron arc lines and the bottom one contains the ultimate lines of most of the elements. The first five sections are illustrated in Figure 3. These ultimate lines, as well as the Fe lines, are drawn while the spectra of the elements are projected on the scale. For this purpose the magnifying and focussing conditions are reproduced by selecting outstanding Fe lines and moving the screen carrier until they fall into coincidence with the lines used to make the scale or until they occupy the positions of their corresponding wave length readings. Wave lengths between $\lambda 2500$



and $\lambda 3300$ as read from this scale are in error by no more than $0.2 \text{ \AA}$, particularly when the line to be identified lies between two close iron lines, since in this case the screen is adjusted so that these lines cut exactly their wave length values on the scale. Then the sought wave length is read directly.

3. Arcing Conditions

In the course of these experiments it was early discovered that the process of arcing samples demands a highly specialized technique. In general samples for chemical analysis may be classified as:

1. Metals or alloys.
2. Reducible salts or oxides of metals.
3. Very volatile salts, oxides or elements.
4. Non-volatile substances not easily reducible.
5. Solutions of substances in classes 2, 3, and 4.

The selection of most suitable size and depth of crater for the various types of samples is of great importance, since an analysis performed under adverse conditions may give entirely misleading results. In the following sections we shall outline the conditions found most favorable for the general classes under the arcing technique employed. Of course another worker using different arcing technique might find other conditions more favorable, but in general the conclusions below are of nearly universal application.

Class 1. Metals and alloys.--If metal samples are placed in craters of small diameter the first stages of arcing heat the particles to fusion temperature and the molten globules coalesce and run to the bottom of the crater. Consequently several minutes of arcing may precede the burning of the sample even if the crater is only a few millimeters deep. Further, with craters of small diameter, when the electrode has finally burned away sufficiently for exposure of the sample it often happens that the electrode continues burning until the retaining walls of the crater are destroyed and the bead of sample rolls off the electrode and is lost. Best results have been obtained by use of $3/16$ or $1/4$ inch electrodes with large shallow craters. Generally with this size electrode the crater is one-half the diameter of the electrode and is about 2-3 mm. deep. With most of the samples employed

burning conditions in such a crater are better when the lower electrode is made the anode. Then the arc usually strikes the bead of sample as soon as this is melted and sample is consumed much more rapidly than electrode. Although there has been a large amount of work emphasizing the advantage of using the cathode for excitation, because of increased spectral sensitivity in the cathode layer, it seems that for many types of sample use of the anode may be advantageous because of the better burning conditions. When burning in the cathode there is apparently an increase in the intensity of background because of simultaneous consumption of sample and carbon. The whole question of cathode vs. anode demands much more exhaustive tests than could be made in this study and further work is planned.

A very intense spectrum can be obtained with 1 mg. of sample when it is burned in a shallow crater. To prevent loss of sample while striking the arc it is best to place the sample in a crater 4-6 mm. deep, strike the arc and run until sample is melted, cool, cut off the crater until the bead is exposed, readjust electrode position and make the exposure. Danger of loss is decreased by bridging the arc with a carbon rod for starting, rather than to touch the electrodes and then separate. The exposure is continued until all the sample is consumed, for small samples, or for about one minute when large samples are used. In all qualitative analyses the slit width is 0.01 to 0.02 mm.

Class 2. Reducible salts and oxides of metals.--With this class the sample is placed in a large deep crater and it is arced until a metal globule is formed at the bottom of the crater. A preliminary exposure is made during this stage if the presence of very volatile constituents is sought. After the sample is melted the arc is interrupted, the electrode cut off in order to expose the bead of sample, and the exposure made as in Class 1.

Class 3. Volatile substances.--Best arcing of volatile substances has been obtained by use of small, deep craters. In extreme cases, where the boiling point is not over 200-500°C the crater should be about 15 mm. in depth. Usually the electrode is 1/8 or 3/16 in. and the crater about half the diameter of the electrode. No conclusive tests have been made to determine the relative value of cathodic or anodic excitation.

Class 4. Non volatile substances which are not reduced in the arc.--Mineral samples of refractory nature are best burned

under conditions such that there is simultaneous consumption of sample and electrode. For such samples the electrode recommended by Strock,⁴ in his discussion of the Glimmschicht method, have been found useful. The electrode is 1/8 in. in diameter and the crater about 1/16 in. or less. No conclusive work has been done in determining the relative value of cathodic or anodic excitation, but here it is probable that the Glimmschicht method is best since it was largely for such samples that the method was developed.

Class 5. Solutions.--The results of this investigation indicate that it is highly desirable to use the sample in the form of a solution whenever this can conveniently be done. The advantages are:

1. Solutions give, when evaporated in the crater, a very uniform distribution of the sample. This distribution promotes uniform arcing conditions. Even with easily reducible substances the use of solutions largely prevents the formation of metallic beads, for the uniformly distributed layer of residue is rapidly evaporated before the reduced particles can coalesce.

2. Many substances exhibit much higher spectral sensitivity when in the form of certain salts than when present as oxide or free element. This appears to be due to the increased volatility of the salts. Of course the anion of the salt must be one which does not decompose to give the oxide, or this advantage is lost. In general the chlorides have been found most useful, since the chlorides of the elements are in general the most volatile stable salts.

3. The rapid arcing obtained with solutions decreases the amount of background in the spectrum because there is little attack of the electrode as long as there is a uniformly distributed layer of salt in the crater. The burning of a sample after evaporation of a solution in the crater follows a regular sequence. When the arc is first started, with the sample in the anode, the sample is rapidly heated to its boiling point. When this happens the resistance of the arc drops, the arc column becomes very steady, and strikes directly into the crater. Burning is very steady, with little wandering of the arc, until most of the salt is gone. At this point the resistance rises and the arc again

⁴L. W. Strock, "Spectrum Analysis With the Carbon Arc Cathode," Adam Hilger, Ltd., London, 1936, p. 25.

strikes the upper edge of the crater. When this happens the arc becomes unsteady and wanders about the edge of the crater. Background intensity rapidly increases if the arcing is continued while electrode is being consumed, probably because of the presence of incandescent carbon particles in the arc (see p. 23).

4. The use of solutions facilitates semi-quantitative estimations because the amount of sample is readily controlled and the conditions for arcing may be made very uniform. For example, in a series of determinations, it was found that residues from a given amount of solution were completely arced in a time of 40-45 seconds and no sample gave an arcing time outside of these limits. The spectral lines of minor impurities in the samples were of very uniform intensity throughout the series of determinations, and it was possible to estimate the amount present quite accurately by visual comparison of the spectra with spectra of samples of known composition.

5. The use of solutions permits addition of arcing aids. For example (vide infra) it was found that addition of a small amount of sodium fluoride to samples containing silica and manganese in a sodium carbonate base was a decided aid in the uniform evaporation of the silica and manganese. It seems probable that in many cases the addition of fluoride or chloride ion will prove beneficial in promoting the uniform evaporation of the various constituents of a sample and prevent excessive fractionation of the constituents.

The technique for the use of solutions has been carefully studied, in connection with quantitative analyses, and complete directions are given in a later section. The preliminary examination of solution samples is made in the same way as for solid samples.

4. Complete Qualitative Spectrographic Examination of a Solid Sample

If a solid sample, of unknown composition, is to be analyzed a preliminary spectrum is first taken with fractional exposures. The sample is placed in a deep crater, the exposure started at a low amperage, and the plate holder is moved at 30 secs. intervals so as to record the lines emitted at various times. When it appears that the sample may have fused and collected at the bottom of the crater the exposure is interrupted,

the crater cut off in order to expose the bead of sample and the fractional exposure continued until the sample is entirely consumed. For the latter portions of the vaporization the amperage is increased to facilitate vaporization of high boiling substances.

The preliminary plate, containing the fractional exposures, is examined before further exposures are made. If it is found that the sample shows the presence of substances volatilized at different rates the various fractions are analyzed by comparison of the spectra with the wave length scales described above. In general this procedure is not desirable, however, because of the difficulty in setting the spectrum, which may contain few lines, into exact coincidence with the wave length scale. If inspection shows that all constituents of the sample vaporize in certain fractions, another exposure is made under such conditions as to insure complete vaporization and an iron arc spectrum is recorded directly above that of the sample, by use of a multi-aperture slit cover, without moving the plate holder. Since the complete vaporization of the sample may require several minutes, the intensity of the light is reduced by a rotating sector placed before the slit.

If the spectrum of a sample is complex, examination may be very tedious. In this case it is preferable to select the major constituents by a preliminary examination of the spectrum and to photograph the spectrum of a mixture containing the identified constituents together with a spectrum of the unknown. Then, by use of the wave length scale, it is a simple matter to identify the lines appearing in the unknown and not in the synthetic standard. Even complex spectra may be analyzed in this way. For example, vanadium was readily identified in small concentration in a mixture containing a large amount of chromium although the chromium spectrum is very complex. In the comparison of the sample with the spectrum of pure chromium many lines were noted that did not appear in the chromium spectrum. All of these agreed in wave length with prominent vanadium lines. Addition of vanadium to the chromium standard gave a spectrum identical to that of the unknown substance.

In few cases is the presence of a single line taken as positive identification of a substance. If the position of a line leads to a tentative identification, this is confirmed or disproved by reference to a table of ultimate lines. When the line

in question may coincide with a given ultimate line the presence of other lines of comparable intensity is sought. If these are not present it is considered positive proof of absence for the element in question. In all cases the possibilities of coincidence are kept in mind and the wave length tables of Kayser⁵ are used to indicate the possibilities for a line found of given wave length.

In all analyses in which there are found appreciable amounts of substances having complex spectra, it is advisable to check the analysis by photographing the spectrum of the sample together with that of a synthetic mixture made up according to the analysis found for the sample. Of course this is possible only when spectroscopically tested portions of the various elements believed to be in the sample are available.

5. Spectral Sensitivity

No exhaustive studies have been made on the ultimate sensitivity of detection of the various elements. The claims made by various authors, using a variety of methods, indicate that in general quantities down to 0.01 to 0.001 may be detected in the most favorable case and that even in unfavorable cases 1 is usually detectable. These correspond to percentages of 0.01 to 0.00001 when 10 mg. of material is arced. Cholak (private communication) gives the following list of amounts detectable in the arc:

Element	Line detected	Amount detectable
Aluminum	3082.16 A ^o	0.02 gamma
Antimony	2598.08	.40
Bismuth	3067.73	.04
Cadmium	3261.05	.40
Chromium	2986.47	.20
Copper	3273.96	.02
Iron	3020.65	.02
Lead	2833.07	.02
Magnesium	2802.71	.02
Manganese	2593.73	.02
Mercury	2536.52	.20
Nickel	3050.83	.40

Several of these have been confirmed in this work and it appears that his estimates are in all cases conservative.

⁵H. Kayser, "Tabelle der Hauptlinien der Linien-spektra aller Elemente," J. Springer, Berlin, 1926.

Various factors influence the sensitivity. Chief among these are:

1. Type of excitation.
2. Presence of deactivating atoms.
3. Presence of anions which increase volatility.
4. Intensity of background.

The effect of type of excitation is related to the voltage drop in the arc column. When this drop is high a greater proportion of the atoms present exist in excited states and emit radiation. Thus spark methods often give higher sensitivity than do arc methods. In a given type of arc the sensitivity varies with the current. In one experiment the intensity of silicon lines was compared at currents of 10 and 15 amperes. The intensity was, for given silicon content, more than doubled when the current was raised to 15 amperes. The increase was attributed to the greater voltage drop across the arc.

Deactivating atoms are those that may, by collisions of the second kind, take energy from an activated atom and cause it to return to its normal state without emission of light. All atoms of low ionization potential may function in this way, thus leading to decreased sensitivity if they are present in large amounts.

The presence of certain anions may lead to increased sensitivity, as explained above. Further tests are planned and more quantitative results will be sought.

Background radiation either as continuous light in the source or as scattered light in the spectrograph, may markedly decrease sensitivity. Because of this it is important to shield the spectrograph from the light of the incandescent electrodes and to insure against stray light in the instrument. In all exposures care must be taken to arc under such conditions that rapid vaporization of sample occurs, and to minimize the period of exposure in which electrode is consumed more rapidly than sample. Thus, much higher sensitivity was obtained for metal samples after it was found that the electrode must be cut off to expose the bead of sample (after this had melted).

CHAPTER III

QUANTITATIVE ANALYSIS

The general methods of quantitative spectrographic analysis have been well established and tested by the numerous researches in the field during the last few years. However, each determination offers special problems and conditions must be carefully established before accurate results can be obtained. The general procedure is as follows:

The sample, in the form of solution, is introduced into the crater of an electrode and evaporated to dryness. A known amount of a suitable element is added to the solution before the aliquot is taken, to serve as internal standard. The dried sample is arced under carefully determined conditions. On each plate there is placed a calibration spectrum which gives a blackening-intensity curve for that particular plate. The ratio of intensity of the unknown line to that of a selected line of standard is determined by measuring the density of the lines with a microphotometer and correcting the microphotometer reading to a relative intensity reading by use of the calibration curve. Then, by use of a previously established line ratio-concentration curve, there is determined the concentration of the unknown substance in the mixture.

Before beginning the study of methods for silica determination, the special objective of this work, the various steps in the standard procedure were separately investigated by use of samples whose analysis has been extensively studied. For this preliminary work the determination of lead was first attempted, but this was soon discontinued because of the prevalence of lead in reagents and glass ware and the study was shifted to bismuth, which is not a common contaminant of reagents.

1. Form of Sample

It is highly desirable that the sample be in the form of a solution because (1) this facilitates accurate measurements of

aliquot portions; (2) preliminary work has shown that conditions in the arc are more reproducible when a solution is dried in the crater than when a powder sample is introduced into the crater. The solution of the sample must usually contain added material to serve as burning aid. If a given ash is dissolved in acid and aliquot portions of the solution are arced it is found that the intensity of a line of a minor constituent may markedly depend upon the composition of the ash. If, however, the solution contains an excess of some readily vaporizable material, known as the base, the effect of fluctuations in composition of the original ash is minimized (due to the large excess of atoms from the base). The base is usually alkali or alkaline earth chlorides and may contain zinc or ammonium chloride to give better burning properties. In any given case the choice of base material depends upon the general composition of the sample, the methods used for bringing the sample into solution, and the volatility of the sought constituent. Before beginning work on a new determination various base materials should be tested, by means of fractional volatilization exposures, for burning qualities and for the uniformity of vaporization of sample and standard.

2. Evaporation of Sample

Perhaps the more important step in the process is the introduction of the sample into the electrode and the evaporation to dryness. In a good evaporation the sample is uniformly deposited throughout the interior of the crater up to a point 1 mm. from the rim. No salt should be visible on the outside of the electrode. Various methods⁶ were tried to prevent penetration, including treating the inside of the crater with kerosene,⁷ but whenever the whole crater was treated it was found that an air bubble was formed beneath the drop of solution, and that this, on rising, caused uneven evaporation. The method finally selected was a treatment of the rim of the crater with kerosene. For this the rim was lightly touched to a filter paper moistened with kerosene. Penetration below the rim was negligible. Solutions of mineral oil in ligroin were also tried, but results were not as

⁶Wilhelm, Ind. Eng. Chem., Anal. Ed., 10, 211 (1938).

⁷Suggested by Dr. J. S. Owens, of Dow Chemical Company.

uniform as with the kerosene.

The sample (up to 0.10 ml. in volume) is introduced into the crater by means of a micropipet. The electrode is cold and the pipet reaches to the bottom of the crater, in order to prevent inclusion of an air bubble. After the sample is added, the electrode is placed in a hole in a steel block and evaporation is conducted at a low temperature. After evaporation the temperature is raised in order to dehydrate most of the salts present.

3. Electrode

Preliminary tests showed that use of a 1/4 in. electrode gave best results for analysis of solutions. Although there is less wandering of the arc in smaller electrodes, the capacity of the crater is so limited that it is difficult to introduce a sufficiently large volume of sample in a single portion. Use of several portions of sample is to be avoided whenever possible because of the possibility of loss and because the evaporation is not as uniform as with a single portion. For most uses the crater is 3 mm. in diameter by 5 to 10 mm. deep.

4. Arcing and Exposure Conditions

Procedures for arcing were tested exhaustively, using fractional volatilization in every case. The procedure found to give most uniform volatilization, greatest freedom from background, and least wandering of the arc, was the following: The lower electrode with sample is made the anode. The cathode is a similar electrode with a crater like that of the anode. Electrodes are accurately set into position before the arc is started, and the arc is struck by momentarily bridging the electrodes with a graphite rod. A current of 10 amp. is used. Within a few seconds of striking the arc it becomes steady and strikes into the anode crater, impinging directly upon the sample. During this period there is little vaporization of carbon but the sample is rapidly and uniformly vaporized. At the end of the arcing, when the sample is gone, the arc again strikes the rim of the anode and begins to wander. The exposure is continued for 10 secs. after this time. The entire exposure requires about 1 min. when the sample is 2-3 mg. of salt. The intensity on the plate is reduced by a

rotating sector set to give about 1800 interruptions per minute. By means of a wedge slit cover the height of the line was made 2.5 mm. By giving 3 mm. to each spectrum 20 spectra may be photographed on a plate 4 x 10 in., in addition to the calibration spectrum.

Each plate carries a calibration spectrum, made by use of a rotating step sector with an iron arc. The step openings are set in the ratio 1 : 2 : 3 : 4, each step having a height of 3 mm. An exposure made without the sector showed that the lines are of uniform intensity from top to bottom. Therefore the intensity ratio in the various steps is exactly that of the sector openings. The sector is operated to give 1800 interruptions per minute, since it has been shown⁸ that rapid interruption reduces the magnitude of the intermittency effect in photographic action of light.

Eastman Process plate is used for all quantitative exposures because of high contrast. The plate is developed, hardened and fixed according to the procedure recommended by the manufacturer.⁹ Drying is done in a dustproof box by blowing filtered air rapidly over the plate. The operation requires about thirty minutes.

5. Photometering

A modification of the photometer described by Dershem¹⁰ was constructed for measuring line blackening on the plates. In order to insure accurate alignment of the narrow spectral lines with the slit of the photometer it was necessary to project an enlarged image of the line onto the slit. A Spencer Delineascope served for illumination and a Zeiss lens was used for formation of the image. The 500 watt lamp of the projector was operated from a 110 volt synchronous motor generator. It was found to give a moderately steady light beam, which was much better than could be obtained by use of current from the power lines of the laboratory. The position of lantern and slit was kept constant, only

⁸Webb, J. Optical Soc. Am., 23, 157-169 (1933).

⁹"Photographic Plates for use in Spectroscopy and Astronomy," Eastman Kodak Company, Rochester, 1937.

¹⁰Dershem, Rev. Sci. Inst., 3, 43 (1932).

the plate being moved during a measurement. The photoelectric current was measured by a Dershem electrometer, operated by the drift rate method. Since the drift rate (time required for the needle to move through a given angle) is inversely proportional to the current it was not necessary to convert photometer readings to photoelectric current, but the time readings were used directly.

A great variety of procedures is employed in converting photometer readings to spectroscopic intensity, but the one employed in this study is accurate, simple, and direct, without necessity for converting readings to logarithms or plotting on log paper. First of all the steps of the calibration spectrum are measured accurately on the photometer. A plot is constructed for photometer time against relative intensity in the steps. A typical calibration curve is shown in Figure 4. Now, by use of this curve, any other photometer reading taken on the same plate may be converted to a relative intensity reading. Only two assumptions are involved: First, we assume that for a given blackening of the plate the product of light intensity by time of exposure is constant. Neglecting possible deviations due to the intermittency effect, this assumption is justified since the iron line used for the plate calibration is selected from the same wave length region as the line to be measured. Secondly, it is assumed that the background is the same for all lines. By proper technique in arcing the sample it is easy to obtain plates of very low background for the ultraviolet region. In case it is found impossible to obtain clean spectra, free of background, it is necessary to use one of the measured lines for the plate calibration and at times to make very elaborate corrections, as described by Strock.¹¹ The procedure employed is open to an objection that only a narrow range of blackness ratios can be covered in a given spectrum, but this is not a serious disadvantage. Few photometers are capable of giving accurate comparisons of two lines if the blackness (number of silver grains developed) is not within a four- to five-fold range. In case comparisons are needed for two lines of widely different blackness it is necessary either to take the spectrum with a step sector and to compare different steps for the two lines, or to take a preliminary exposure and by

¹¹L. W. Strock, "Spectrum Analysis With the Carbon Arc Layer," Adam Hilger, Ltd., London, 1936, p. 40.

Plate Characteristic Curve

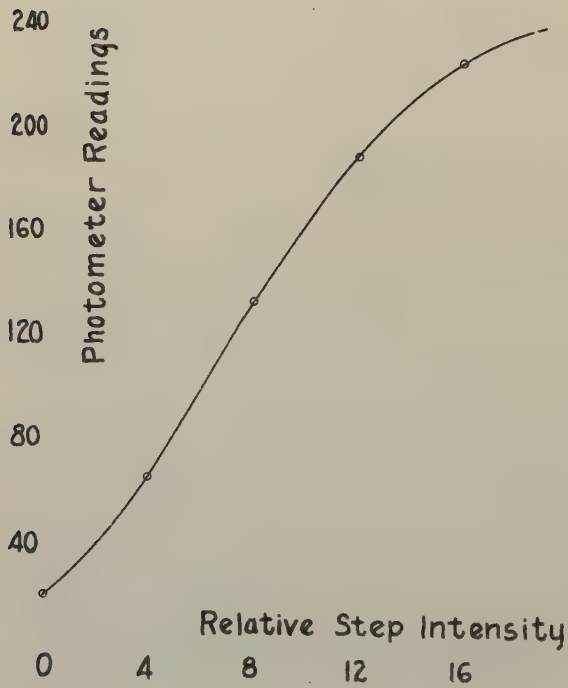


Fig. 4

dilution change conditions so that the final exposure will provide proper conditions for the comparison lines.

6. Calibration Curve for Analysis

The first stage in quantitative spectrographic analysis, after preliminary investigation to ascertain the proper type of sample, internal standard, exposure conditions, etc., is to prepare a calibration curve. This curve may be drawn on either a direct or logarithmic scale, but the former is preferred since it more directly indicates the expected precision from analyses. To prepare the calibration curve a series of spectra are taken with various known concentrations of the substance to be analyzed and a fixed concentration of the substance to be used as internal standard. After photometering, the blacknesses of the various lines are reduced to relative intensity readings and the ratio (intensity of sample line) : (intensity of standard line) is plotted against the absolute amount of sample present in the arc. A typical curve is shown in Figure 5. In case it is desired to extend the range of the analysis beyond the point where a given line shows little variation in blackness with change in concentration, it is often convenient to shift the comparison to another line of the sample which has less intensity. Another alternative is to use a stepped spectrum and to compare various steps, as mentioned above.

Standard Curve for Silica Determinations

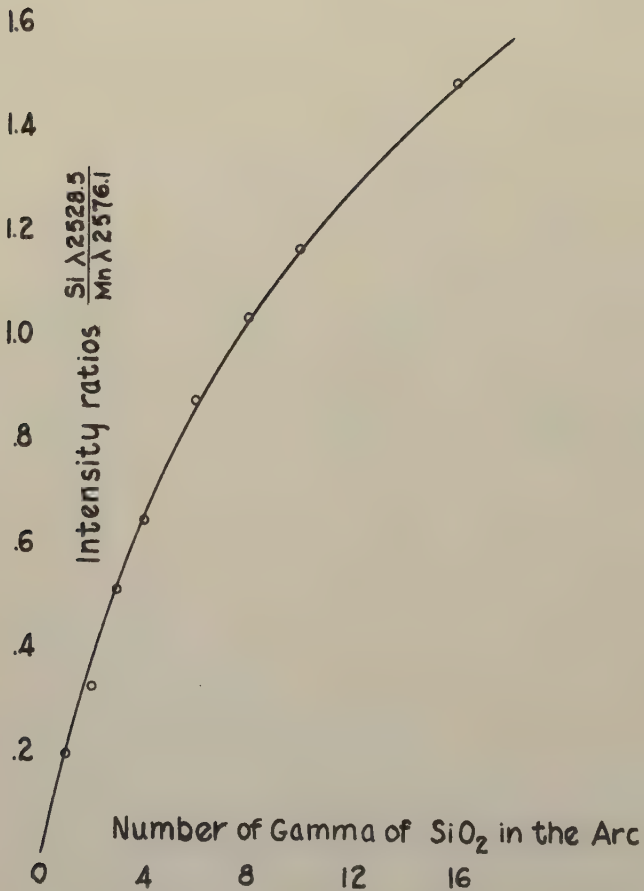


Fig. 5

CHAPTER IV

QUANTITATIVE DETERMINATION OF SILICA

There were several reasons for the choice of silica as a typical example for critical study of quantitative spectrographic analysis. First of all there is a growing realization of the importance of silica in respiratory diseases and a need for an analytical method that may be accurately applied to the analysis of small amounts. Secondly, there are no good chemical methods for the determination of small amounts. The gravimetric method, followed by volatilization of silica as the tetrafluoride, may be adapted to a micro scale, but the operation is very tedious and is subject to many errors. A colorimetric method has been worked out, based on the precipitation of a molybdate and colorimetric estimation of the molybdenum, but this has two serious drawbacks; the intensity of color is small, and it is necessary to remove phosphorus without loss of silica. Finally, it is felt that if a good spectrographic method is established, this method may be used as a control to facilitate the study of chemical methods having sufficient accuracy and convenience.

The immediate objective for this study is an application of the spectrographic method to the analysis of sputum samples from silicosis patients, in conjunction with the Chicago Municipal Tuberculosis Sanatorium. The method, therefore, is based upon detection of the amounts of silica that may be present in 200 mg. of dry sputum. Since at the outset the composition of the sample and the possible interfering substances are not known it is felt that the sample should be fused with sodium carbonate to give a solution free of heavy metals.

1. Preparation of Samples

The ash corresponding to 200 mgs. of the dry tissue, sputum or other biological material is fused in a platinum crucible with 100 mgs. of pure sodium carbonate. The melt is taken up with water, washed into a 5 ml. volumetric flask and diluted to the

mark. Of this, aliquot portions of 0.05 ml. each are taken for analysis.

As base material a mixture of sodium fluoride and sodium carbonate is used. The latter substance is incorporated during the preparation of the sample. The sodium fluoride and the internal standard, manganese as potassium permanganate, are kept in solutions of the appropriate concentrations and are mixed with the sample just before its introduction into the electrode crater. The sample arced contains 0.5 mg. of sodium fluoride, 1.0 mg. of sodium carbonate, 0.8 gamma of manganese and an amount of silica anywhere between 1 and 20 gamma. A base material is employed to insure steady burning and to aid the complete volatilization of the silica within a relatively short time. For this purpose sodium chloride, calcium chloride, magnesium chloride, sodium phosphate, potassium acid fluoride and calcium fluoride were tried, but they were found not to be as good as the mixture of sodium fluoride and sodium carbonate described above.

2. Internal Standard

Manganese, in the form of potassium permanganate, was selected as the preliminary internal standard. It shows three very persistent lines close to the characteristic group of six silicon lines in the region $\lambda 2500$ to $\lambda 2600 \text{ A}^\circ$. For intensity comparison the manganese line $\lambda 2576.1$, and the silicon line $\lambda 2528.5$ are used. Manganese fulfills one of the most important requirements of an internal standard. Its behavior in the arc as determined by a series of fractional spectra of 10 sec. intervals each is identical to that of the silicon. Both elements volatilize during the burning period occurring between 20 th and 45 th sec. after striking the arc. Furthermore, the permanganate ion is fairly stable in the alkaline solutions employed in this determination.

3. Preparation of Electrodes and Spectrographic Technique

By means of a 0.10 ml. pipet 0.07 ml. of the prepared solution sample is transferred to the electrode crater, 3 mm. in diameter and 7 mm. deep. The tip of the pipet should touch the bottom of the crater and the solution should be delivered very slowly to insure the exclusion of air bubbles. Four electrodes are filled

for each sample. Evaporation is conducted in the manner described in Chapter III of this study.

For making the exposures, the lower electrode, which is made the anode, is set to the height of the alignment pointer. The cathode is then adjusted so that the separation between the electrode is 5 mm. The arc is started by the bridging method. About $\frac{3}{5}$ of the arc column is allowed to pass through the screen and the radiations, reduced to $\frac{1}{8}$ by means of the rotating sector, fall on a slit 2.5 mm. in height and 0.05 mm. wide. The exposures are continued for 10 more sec. after the sample has been completely volatilized. Complete volatilization, indicated by the hissing of the arc, is usually attained in 50 sec.

An (intensity ratio) - (silica concentration) curve is prepared from a series of spectra of standard solutions. The standard silica stock solution, containing 1 mg. of SiO_2 per ml., is prepared by fusing the proper amount of pure ignited silicic acid with eight times its weight of pure anhydrous sodium carbonate, dissolving in water, and completing to the required volume. This solution as well as those of sodium fluoride and of sodium carbonate are kept in ceresin wax bottles. The standard solutions used contain the proper amount of the internal standard, base material and 1, 2, 3, 4, 6, 8, 10, 13, and 16 gamma of silica, respectively, per 0.07 ml. Each solution is prepared just before it is transferred to the electrodes. Six spectra of each solution are photographed and a set of three plates is taken for each set of standards.

Care must be taken to develop all plates under identical conditions. Fresh developer must be used for each plate, and temperature and time of development must be carefully controlled. Use of a hardening bath is recommended, especially in hot weather.

4. Treatment of Results

Although the photometer light source was as steady as can usually be obtained with a 500 watt lamp, it was found that there is a constant drift over a period of time. To correct for this it is necessary to check the light intensity by frequent readings on a plate of standard blackness. Before photometering a plate the source and slit width are adjusted to give a drift rate time of approximately 75 (all readings are given in units of 0.1 sec.) then all readings taken on a plate are corrected to this value by

multiplying with the factor:

$$F = \frac{\text{observed drift time of standard at beginning}}{\text{drift time for standard at time of observation}}$$

This procedure is valid because the drift rate time is inversely proportional to the light intensity at the slit.

The data obtained for silica are shown in the following tabulation and are represented in various methods in Figures 4, 5, 6, 7, and 8.

In the tabulation the first column gives the observed drift rate time in 0.1 sec. units. The second column gives corrected time, now multiplied by a factor of two to facilitate plotting on the desired scale. The third column gives the intensity of the lines in relative units. This intensity is obtained from the plate characteristic curve, constructed by use of a stepped iron arc spectrum as described on page 25. The fourth column gives the ratio of intensity of silica line to the selected manganese line. Finally, the deviations of the individual results are shown.

One marked deviation was made from standard practice in this series of comparisons. After several plates had been measured it became apparent that the plate characteristic curves were all practically identical except for shifts in the ordinates. Accordingly it was felt that more accurate results might be obtained by use of a composite plate characteristic curve than by individual curves for each plate. Such a composite curve was used in the above tabulations.

The average values of line ratio are plotted in Figure 5 as a function of the number of gamma silica present. This is the standard curve on which all future analyses are based. To get a clearer idea of the expected variations in actual analyses, a curve was constructed to show the deviations. In this curve, Figure 6, each individual determination is represented by a point. Identical points are indicated by displacing succeeding ones one millimeter to the right of the preceeding one. From this curve it is seen that maximum deviations are large, but that good results are obtained from most of the individual determinations. The average of a number of determinations appears to be quite reliable.

The reliability of the results is more clearly demonstrated in the following tabulation, which expresses average deviations in

Silica in the Arc	Photometer Readings		Corrected Readings		Relative Intensity		Ratio Relative Intensities	Deviations From the Average
	Si 2528.5	Mn 2576.1	Si	Mn	Si	Mn	Si:Mn	
1 gamma	17	55	37	119	170	717	(0.24)	(0.05)
	15	57	33	123	126	740	.17	2
	16	55	35	119	150	717	.21	2
	16	54	35	117	150	705	.21	2
	16	55	35	119	150	717	.21	2
	15	53	33	113	126	684	.18	1
	19	66	32	113	120	685	.18	1
	18	67	31	114	110	690	.16	3
	18	56	31	96	110	587	.19	0
	19	65	32	111	120	672	.18	1
	17	47	29	80	93	496	.19	0
	19	55	32	94	120	580	.21	2
	Average						.19	.015
2 gamma	19	54	39	111	188	672	0.28	0.04
	22	56	45	115	240	695	.35	3
	20	49	41	101	203	615	.33	1
	20	54	40	111	197	672	.29	5
	20	46	41	94	203	580	.35	3
	Average						.32	.028
3 gamma	24	56	51	119	290	717	(0.40)	(0.07)
	26	54	54	115	313	695	.45	5
	28	59	60	126	360	756	.48	2
	26	56	56	119	325	717	.45	5
	27	53	58	113	340	684	.50	0
	28	58	59	124	350	745	.47	3
	38	68	61	109	367	662	.55	5
	35	70	56	112	330	680	.49	1
	34	69	55	110	317	670	.47	3
	37	64	59	102	350	622	.55	5
	34	65	55	104	330	635	.52	2
	37	66	59	106	350	646	.54	4
	Average						.50	.032
4 gamma	29	55	62	117	374	705	0.53	.11
	33	52	70	111	430	672	.64	0
	39	56	83	119	514	717	.72	8
	38	54	81	115	500	695	.72	8
	30	51	64	109	390	662	.59	5
	Average						.64	.064

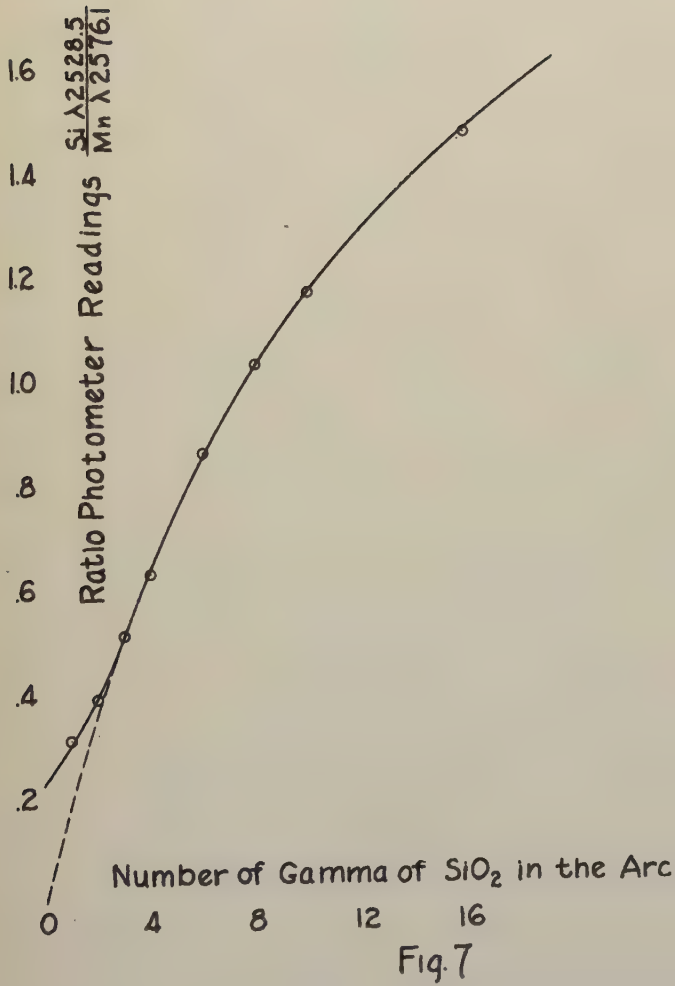
terms of amounts of silica. This table shows the accuracy to be expected in an analysis made with four or more samples.

No. of Samples	SiO ₂ in Arc	Average Deviation (SiO ₂)
11	1	0.08
5	2	.18
11	3	.25
4	4	.40
11	6	.25
5	8	.65
11	10	.60
4	16	1.05

To test the value of using the plate characteristic curve, a curve was constructed from the ratios of the photometer readings of the lines, without correction for plate characteristic. This curve was found to be practically identical with the corrected intensity ratio curve of Figure 5, except in the region of low concentration. The uncorrected curve is shown in Figure 7. An obvious deduction from a comparison of the curves is that in regions of moderate intensity, where the characteristic plate curve is nearly straight there is no necessity for correction of photometer readings to relative intensity, but where the characteristic curve is far from straight, better results are obtained by correction of photometer readings to intensity.

A plot of individual determinations, expressed as the photometer readings for the silica line, is shown in Figure 8. A comparison of this curve with the one showing the ratio of line intensity to that of the internal standard shows that while quite good results could be obtained merely by making all exposures under carefully controlled conditions and measuring the blackness of the silica line, it is more accurate to use an internal standard since the variations of the individual photometer readings are quite high. These variations are indicated in Figure 8, in the way explained for Figure 6.

Photometer Readings Ratio Curve



Silicon Blackness Curve

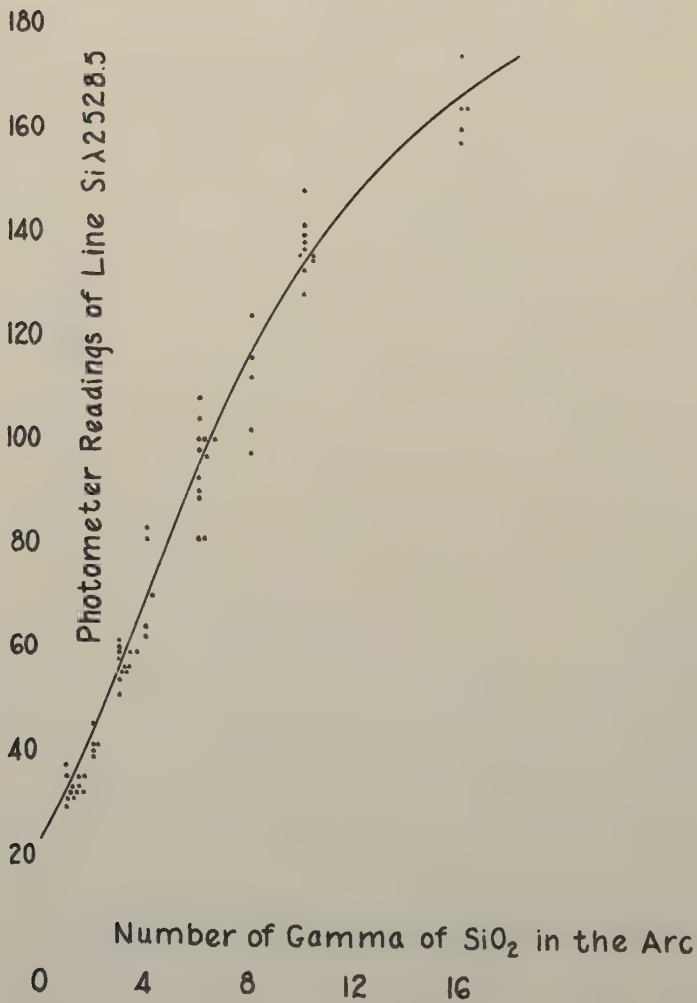


Fig. 8

SUMMARY

This investigation is confined to applications of the d.c. carbon arc for general chemical analysis. Available spectrographic equipment is discussed. A rapid method for the identification of the elements by means of projecting the spectrum of the sample onto a chart containing the ultimate lines of the common metals, the most important lines of the iron arc spectrum, and a large scale of wave lengths is developed. Methods for arcing various types of samples and the proper size of electrode and depth of crater for best results with each sample are given. A general procedure for quantitative spectrographic analysis is discussed, in which the stepped iron arc spectrum is used as blackening marks for the calibration of each plate. The introduction of sample in the form of solution into the crater of the electrode and the subsequent evaporation of this to dryness is advocated. A method for the quantitative determination of silica in biological materials is developed. The method consists in fusing the ashed material with sodium carbonate. The melt is dissolved in water and an aliquot portion is mixed with sodium fluoride and potassium permanganate, where manganese is used as internal standard. The spectrum of the evaporated solution is taken, the ratio of the intensity of a silicon line to that of a manganese line is determined microphotometrically and from a previously established line ratio-concentration curve the amount of silica in the arc is ascertained.

